# Applicability of the Homogeneous Nucleation Theory to the Condensation in Free Gas Expansions

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**Abstract.** The traditional application of the classical homogeneous nucleation theory (CNT) to the condensation in rapidly expanding flows involves the use of the steady-state nucleation rate. Since this rate is derived under the assumption of both steady-state and isobaric/isothermal conditions, the applicability of CNT to highly nonequilibrium environments may be questionable. In addition, the usual strategy of CNT – gas dynamics coupling violates the original nucleation theory even in the isothermal/isobaric environment. In this study, we consider condensation in jets freely expanding into a vacuum. Using the isentropic solution, we approximate the time-dependent pressure and temperature in a given small volume of a gas that is moving along the jet axis with the flow velocity. Several possible strategies of CNT implementation are considered within this volume. It is shown that the terminal cluster distributions are strongly affected by the steady-state assumption and that the original CNT rate equations should be integrated into a computational scheme to model the coupled condensation flow.

## INTRODUCTION

Recent technological advances on the micro- and nano-scale highlight the importance of processes of formation and evolution of liquid/solid drops (clusters) in highly non-equilibrium gas or plasma environments. A theory, capable of providing detailed information on cluster formation and evolution in terms of non-equilibrium spatial distributions of cluster size along with cluster internal and kinetic energies, is highly desirable because experimental investigations of these distributions are usually not possible. The simplest example of such nonequilibrium environment is a free gas expansion formed, e.g., in laser ablation [1], in surface vaporization due to a meteorite strike [2] or in supersonic jets [3]. Traditionally, the classical homogeneous nucleation theory (CNT) [4] based on equilibrium thermodynamics has routinely been applied to the condensation during free gas expansions. However, since the main CNT result, nucleation rate, is derived under the assumption of steady-state conditions in the isobaric/isothermal environment, the applicability of CNT to a highly nonequilibrium environment may be questionable [5].

Although several researchers attribute the cluster formation to the density fluctuations which occur in a thermo-dynamical system at non-zero temperature [6]-[7], the traditional CNT considers clustering as the process of unimolecular reactions of sticking and evaporation among the monomers and clusters. The reaction rates are independent of the isobaric/isothermal assumption [8], therefore, the corresponding rate equations are original while the steady-state nucleation rate calculated from them is derivative. Errors, resulting from the coupling of such rate equations with the gas-dynamics equations are only due to the reaction models. The traditional practice of coupling CNT and gas dynamics, however, is based on the use of the steady-state nucleation rate instead [1], [2], [9]-[11]. It is our goal to show that the traditional approach may lead to significant errors in addition to the errors related to the rate models. The paper is organized as follows. The next Section gives on overview of CNT and discusses a correction factor for the steady-state nucleation rate. The implementation of CNT to isobaric/isothermal environment is discussed in the following Section. The traditional methodology of adding clusters of critical size with the steady-state nucleation rate is shown to be faulty even in this case. In the subsequent Section, the original CNT rate equations coupled with the isentropic-expansion equations are solved numerically for two practical examples, and the solutions are compared with those derived using the conventional approach of the CNT-gas

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dynamics coupling. The concluding Section summarizes the main results. An alternative scheme is proposed since the direct coupling of the rate equations to the full gas-dynamics equations would be computationally intensive.

## CLASSICAL NUCLEATION THEORY

The original CNT rate reactions include sticking of a monomer with another monomer or a cluster and evaporation of a monomer from a cluster. This formulation, though attractive due to its simplicity, is physically unrealistic, because, e.g., two monomers cannot stick together and form a stable dimer unless there is an energy loss mechanism, such as the interaction with a third monomer [3], [12], [13]. Yet, since our goal is not the improvement of CNT but the analysis of its implementation, we will use these over-simplified reactions in the reminder of the paper.

If $N_i$ is the concentration of clusters containing $i$ monomers ($i$-clusters), the CNT rate equations can be written as follows:

$$\frac{dN_i(t)}{dt} = C_{i-1}N_{i-1}(t) - (C_i + E_i)N_i(t) + E_{i+1}N_{i+1}(t); i = 2,3,... \tag{1}$$

where $C_i$ is the rate of monomer sticking with an $i$-cluster or the *condensation rate* and $E_i$ is the rate of monomer evaporation from an $i$-cluster. In the original isobaric/isothermal CNT formulation these rates are constants, but in the non-equilibrium environment they can be time-dependent. Since CNT considers only the initial stage of cluster condensation, where the total cluster mass is small as compared to the vapor mass, it is assumed that the monomer concentration is constant:

$$\frac{dN_1(t)}{dt} = 0 . \tag{2}$$

Also, to make the set of equations (1)-(2) solvable, it is assumed that clusters larger than $G$-clusters are instantly decomposed into monomers, so that

$$\frac{dN_G(t)}{dt} = C_{G-1}N_{G-1}(t) - (C_G + E_G)N_G(t)$$
$$\frac{dN_i(t)}{dt} = 0, \ i > G \tag{3}$$

It can be shown [14] that for sufficiently large $G$ the solution of eqs. (1)-(3) is independent of G.

In order to solve the set of rate equations (1)-(3), CNT considers the free energy barrier, $\Delta F$, in the transition from system vapor state to the liquid state. This barrier is associated with the creation of a new surface and, in the liquid drop approximation [15], is given by

$$\Delta F = 4\pi r^2 \sigma - \frac{4}{3}\frac{R}{\mu}\pi r^3 \rho T \log(S). \tag{4}$$

Here, $r$ is the radius of the freshly nucleated cluster, $\sigma$ its surface tension per unit area, $\rho$ is the liquid density, $R$ is the gas constant, $\mu$ is the molar mass, $T$ is the cluster temperature which is assumed to be the same as the vapor temperature, and $S$ is the supersaturation ratio defined as the ratio of the vapor pressure to the saturation pressure. The energy barrier, eq. (4), has a maximum at a certain cluster radius $r_*$, therefore, once a cluster of this critical size has been formed, its further growth is energetically favorable while the smaller clusters will preferentially decay. Microscopically, the favorableness of the further cluster growth or decay can be expressed by the relation between the condensation and evaporation rates: for clusters smaller than the critical cluster, the evaporation rate exceeds the condensation rate and vice versa. An important conclusion from the energy consideration is that the evaporation rate of a cluster at a given temperature equals the condensation rate of this cluster at the same temperature and such a vapor pressure that the cluster is critical at it. The condensation rate can be estimated using the liquid drop model or by evaluating the sticking cross-sections.

Once the condensation and evaporation rates are defined, the set of rate equations (1)-(3) can be solved. Eqs. (1)-(3) may be written in the matrix form:

$$\frac{d\vec{N}(t)}{dt} = \mathbf{A}\vec{N}(t).$$
(5)

The exact solution is then given by

$$\vec{N}(t) = B_1 \exp(\lambda_1 t)\vec{q}_1 + B_2 \exp(\lambda_2 t)\vec{q}_2 + ... + B_G \exp(\lambda_G t)\vec{q}_G,$$
(6)

where $B_i$ are constants defined by the initial conditions, $\lambda_i$ and $\vec{q}_i$ are the eigenvalues and eigenvectors of matrix $\mathbf{A}$. Since matrix $\mathbf{A}$ is not diagonal, its eigenvalues and eigenvectors can only be evaluated numerically. It can be shown that $\lambda_i \leq 0$, so that the concentrations $N_i$ will eventually reach steady values. The transient time needed for the system to arrive at the steady state can be roughly approximated by the inverse of the minimal non-zero $\lambda$. Note that the so-called lag time in CNT has a slightly different definition and there exist analytical expressions to calculate it [16], [17].

CNT offers an approximate analytical solution for the steady state case. To get the solution, let us rewrite eq. (1) in the following "current" form:

$$\frac{dN_i(t)}{dt} = I_{i-1}(t) - I_i(t); \ i = 2,3,...,G,$$
(7)

where the currents $I_i$ are given by

$$I_i(t) = C_i N_i(t) - E_{i+1} N_{i+1}(t); \ i = 2,3,...,G-1$$
$$I_G(t) = C_G N_G(t)$$
(8)

The physical meaning of $I_i$ is the number of freshly formed $i$-clusters per unit volume and time. Next, the following quantities are introduced:

$$D_i = N_1 \exp\left(-\frac{\Delta F_i}{kT}\right),$$
(9)

where $\Delta F_i$ is calculated from eq. (4) using $r=r_i$. The physical meaning of $D_i$ is the number density of $i$-clusters at a total equilibrium (not just at a steady state) if it were possible. The important feature of $D_i$ is that for $i \gg 1$

$$\frac{D_i}{D_{i+1}} \approx \frac{E_{i+1}}{C_i},$$
(10)

In the steady state all currents are equal and eqs. (8) can be rewritten using eq. (10) as follows:

$$\frac{I_{ss}}{C_i D_i} \approx \left(\frac{N_i}{D_i} - \frac{N_{i+1}}{D_{i+1}}\right).$$
(11)

In eq. (11) $I_{ss}$ is the steady-state current. By summing eq. (11) over all $i$, we have

$$I_{ss}\left(\frac{1}{C_1 D_1} + \frac{1}{C_2 D_2} + ... + \frac{1}{C_G D_G}\right) = \frac{N_1}{D_1}.$$
(12)

The next approximation is due to the fact that the condensation rate weakly depends on $i$ and that $D_i$, as defined in eq. (9), has a sharp minimum at a critical size $i^*$. Treating $i$ as a quasi-continuous variable and using the 3-term Taylor expansion, the sum in eq. (12) can be approximated by

$$\left(\frac{1}{C_1 D_1} + \frac{1}{C_2 D_2} + ... + \frac{1}{C_G D_G}\right) \approx \frac{1}{C_{i*}} \sum_{i=1}^{G} K_1 \exp\left[-K_2(i-i^*)^2\right],$$
(13)

where $K_1$ and $K_2$ are constants. The exponential sum in eq. (13) can be approximated by an integral and the final expression for the steady-state nucleation rate $I_{ss}$ has the following form:

$$I_{ss} \approx \frac{1}{\rho}\sqrt{\frac{2\sigma m}{\pi}} N_1^2 \exp\left(-\frac{4\pi r_*^2 \sigma}{3kT}\right)\frac{N_1}{D_1} = I_{CNT}\frac{N_1}{D_1}.$$
(14)

Eq. (14) is approximated because both eq. (10) and eq. (13) are approximated. The relation, eq. (14), differs from the usual expression for the nucleation rate by the last term, $\dfrac{N_1}{D_1}$. By some vague arguments [14], CNT assumes that this term is just unity [14]; however, the "equilibrium" concentration of monomers $D_1$, formally calculated by eq. (9) may differ from $N_1$ by several orders of magnitude. Its value is given by the following correction factor,

$$\frac{N_1}{D_1} = \exp\left(\frac{\Delta F_1}{kT}\right). \tag{15}$$

Note that this factor has a form which is close to the empirical correction factor for water condensation [18]. Note also, that the Kantrowitz correction factor used in [9] only accounts for the heat transfer between the vapor and the clusters and is of the order of unity while both our and empirical correction factors can reach several orders of magnitude, as we will see further.

## APPLICATION OF CNT TO ISOBARIC/ISOTHERMAL ENVIRONMENT

The traditional strategy of CNT application to the non-equilibrium environment is based on the use of the steady-state nucleation rate calculated using the local pressure and temperature at each time instant. All the above-mentioned works [1], [2], [9]-[11] implement time discretization to solve the gas-dynamics equations so that clusters of local critical size are being added with the local nucleation rate to the computational domain at each time step. The somewhat subtle justification for the adding of clusters of critical size and not smaller clusters is that the critical-size clusters will preferentially grow further while the smaller clusters will preferentially decay.

In this Section we show that this strategy results in an incorrect terminal cluster distribution even in the isobaric/isothermal environment. Adding clusters of critical size with the steady-state nucleation rate will modify the original CNT rate equation system (1) as follows:

$$\frac{dN_i(t)}{dt} = C_{i-1}N_{i-1}(t) - (C_i + E_i)N_i(t) + E_{i+1}N_{i+1}(t); i = 3, 4, \ldots i \neq i^*$$

$$\frac{dN_2(t)}{dt} = -(C_2 + E_2)N_2(t) + E_3 N_3(t) \tag{16}$$

$$\frac{dN_{i^*}(t)}{dt} = C_{i^*-1}N_{i^*-1}(t) - (C_{i^*} + E_{i^*})N_{i^*}(t) + E_{i^*+1}N_{i^*+1}(t) + I_{ss(CNT)}$$

In the modified equation set (16), it is assumed that the reactions of condensation and evaporation for the formed clusters are fully addressed in a computational scheme. Analyzing eq. (16), one can see that it differs from the original eq. (1). The main difference is the presence of the source term in the equation for the critical clusters which may lead to the under-representing of smaller clusters and over-representation of large clusters in the terminal distribution. This problem, however, can be eliminated by moving the source term to the equation for dimers. The modified equation which keeps the similarity with eq. (1) is then given by

$$\frac{dN_2(t)}{dt} = I_{ss} - C_2 N_2(t) + E_3 N_3(t) \tag{17}$$

That is, an accurate strategy of adding clusters into the computational domain is the adding dimers with the corrected rate $I_{ss}$, eq. (14), while artificially canceling their evaporation rate.

Let us illustrate these points on the following example. We consider Argon gas at temperature of 48.4 K and at pressure of 595.3 Pa. The reason of choosing this case is that it corresponds to one of the prospective non-equilibrium cases considered in the next Section. Since at temperature of 48.4 K the condensing phase is solid, we estimate the saturation pressure by the equilibrium gas-solid pressure at this temperature [19]. The corresponding supersaturation ratio is 29.3 and the critical cluster size is ten. The last estimate is based on density of 1600 kg/m$^3$ and surface tension of 0.0125 n/m$^2$ of solid Argon.

To make a comparison between the different strategies of CNT implementation, the original set of rate equations (1)-(3) is solved numerically using MATLAB. Instead of calculating the inverse matrix as is suggested in eq. (6), the ODE23tb MATLAB solver for stiff problems [20] is implemented. The reason to obtain a numerical solution is that in the following Section the non-equilibrium problem, for which no matrix solution is available, will be considered.

Similarly, equation systems modeling different strategies of adding clusters with the steady-state nucleation rate are also solved. The considered strategies are (i) adding critical-size clusters with the CNT rate, (ii) adding critical-size clusters with the rate (14) using the correction factor, eq. (15), (iii) adding dimers with the corrected rate, eqs. (14)-(15), and (iv) adding dimers with the corrected rate and canceling evaporation from dimers, eq. (17).
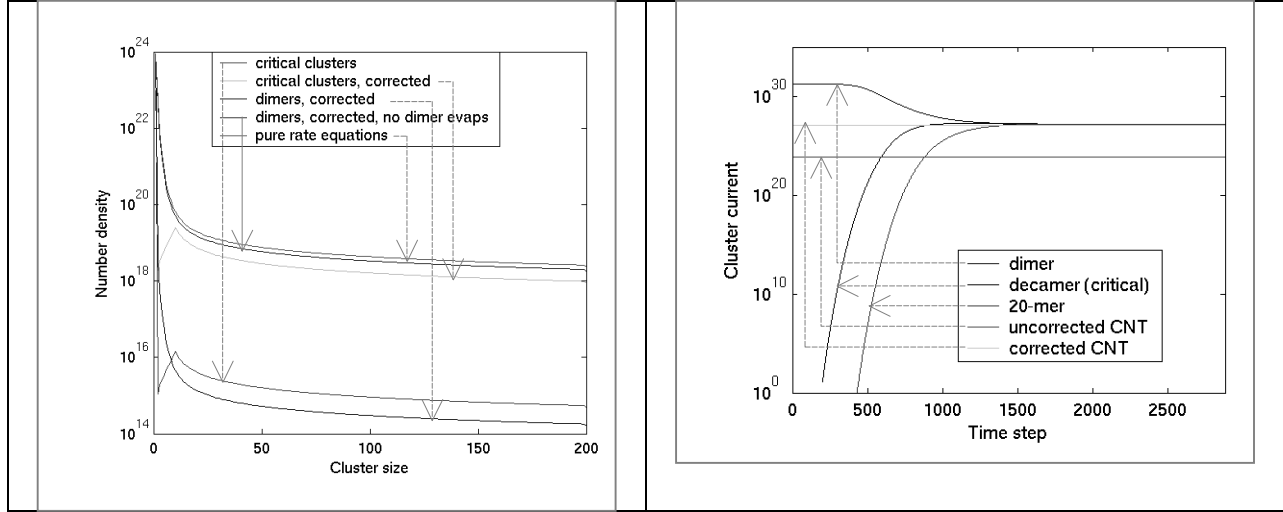


**Fig. 1**. Terminal cluster size distribution (a) and calculated cluster currents (b). Critical size is ten. For explanation, see text.

Fig. 1a shows the results of these strategies. It is seen in the figure that the straightforward strategy of adding critical clusters with the original nucleation rate distorts both terminal cluster concentration and the cluster distribution shape. As expected, small clusters are under-represented in this strategy. The usage of the correction factor, eq. (15) significantly improves the terminal cluster concentration while the distribution shape remains distorted. The proposed strategy of adding dimers with the corrected rate while canceling evaporation from dimers results in the terminal cluster distribution which is practically coincides with that calculated for the original rate equations. Canceling the evaporation from dimers is important in this case as can be seen on the corresponding curve.

Fig. 1b represents the actual cluster currents calculated from the solution of the original rate equations (1)-(3). All calculated rates reach the steady-state value which is practically coincides with the CNT approximate value, eq. (14), corrected by the correction factor, eq. (15). We can conclude that the quadratic approximation, eq. (13) is valid for relatively small critical clusters, such as decamers in our example. One important property of the actual currents is that the initial value of the dimer current is several orders of magnitude larger than the steady-state value. This feature will facilitate explanation of the following non-equilibrium examples.


## APPLICATION OF CNT TO FREE GAS EXPANSIONS

Complete representation of the condensation in free gas expansion is beyond the scope of this paper, which is to reveal the problems of the traditional coupling of CNT to gas dynamics. As a simple yet meaningful approximation we consider a small volume of a gas moving along the jet axis in the supersonic expansion into a vacuum. The gas in this volume will expand and get cooler with time. At a distance of about one nozzle diameter the flow velocity reaches its terminal value and the flow expansion can be approximated by the isentropic formulae [5]

$$\frac{T(x)}{T_0} = K_1(\gamma)\left(\frac{x}{d}\right)^{2-2\gamma}; \frac{P_0}{P(x)} = \left(\frac{T_0}{T(x)}\right)^{\frac{\gamma}{\gamma-1}}; x = vt = \sqrt{\frac{\gamma k T_0}{(\gamma-1)m}}\, t\,. \tag{18}$$

where $\gamma$ is the specific heat ratio, $P_0$ and $T_0$ are the stagnation pressure and temperature, $m$ is the molecular mass, $d$ – nozzle diameter, $x$ – distance from the nozzle along the jet axis and $K_1$ is a constant. It follows from eq. (18) that the vapor number density, $N_1$, in such expansion is subject to

$$\frac{dN_1(t)}{dt} = -\frac{2}{t}N_1(t)\,. \tag{19}$$

Assuming that the cluster concentration is small as compared to that of monomers, the time derivative of the number density of clusters of a given size in the considered volume will be the subject to an additional rarefication term (19), while local temperatures can still be calculated by eq. (18) if we neglect the heat transfer. Similar to the isothermal/isobaric case, we consider three different strategies, (i) direct implementation of rate equations, (ii) adding of critical clusters with the uncorrected CNT nucleation rate, and (iii) adding of dimers with the corrected CNT rate, eqs. (14)-(15) while canceling evaporation from dimers. The corresponding systems of differential equations are given below.

The first strategy is represented by

$$\frac{dN_i(t)}{dt} = C_{i-1}(t)N_{i-1}(t) - (C_i(t) + E_i(t))N_i(t) + E_{i+1}(t)N_{i+1}(t) - \frac{2N_i(t)}{t}; i = 2,3,...,G-1$$

$$\frac{dN_1(t)}{dt} = -\frac{2N_i(t)}{t} + 2E_2(t)N_2(t) + E_3(t)N_3(t) + ... + E_G(t)N_G(t) -$$
$$- 2C_1(t)N_1(t) - C_2(t)N_2(t) - ... - C_G(t)N_G(t)$$

$$\frac{dN_G(t)}{dt} = -\frac{2N_G(t)}{t} - [E_G(t) + C_G(t)]N_G(t) + C_{G-1}(t)N_{G-1}(t)$$

(20)

Here, $G$ is such a (large) number that $N_G$ is negligibly small. The initial conditions for system (20) are

$$N_1(t_0) = \frac{P(t_0)}{kT(t_0)}; N_i(t_0) = 0, i = 2,3,...,G,$$

(21)

where $t_0$ is defined as the time required for the considered small gas volume to travel from the orifice downstream such that local supersaturation occurs, i.e., $S=1$ at time $t_0$. The second and third strategies modify the equations in accordance with eqs. (16)-(17). For brevity, these equations and not given here.

Our first numerical example represents an expansion of water vapor in a rocket thruster plume [19]. Using the available CFD solution for the non-condensing expanding flow [19], we first make sure that the isentropic equations (19) are valid in the region where the condensation may start. Then, the equation system, eqs. (20)-(21) and the equation systems representing two other strategies, are solved numerically using MATLAB software as explained in the previous Section.

The resultant distributions of cluster size are shown in Fig. 2a. For the traditional strategy, the underlying distribution has a clear maximum, or a distribution *mode*, at a cluster size of about 500, which is consistent with our previous solution [19]. However, both direct and dimer-adding strategies result in a different, monotonic distribution shape. To understand the difference, the critical cluster size and the prospective sizes of the introduced dimers in the direct and CNT schemes are plotted along the jet center line in Fig. 2b. Also, the actual, CNT- and CNT-corrected nucleation rates are plotted in Fig. 2c.

It is seen in Fig. 2b and 2c that the differences between the strategies result in both different cluster currents and monomer densities. In the traditional CNT scheme the consumption of monomers is not as high as in the direct and CNT-corrected schemes, therefore, in the traditional CNT scheme a cluster will grow to a greater extent than in the direct and corrected schemes, as seen in Fig. 2b. In the traditional scheme, new clusters are no longer added if the critical size is just one and lower, therefore, the nucleation region in the traditional scheme is located between the distances of about 2 to 3 m from the nozzle. The CNT rate in this region steeply increases becoming somewhat significant at a distance of 2.6 m. The maximum CNT rate occurs at the downstream limit of the nucleation region, where the critical clusters are dimers. According to Fig. 2b, these dimers will eventually grow up to 500-mers, which corresponds to the CNT distribution mode as seen in Fig. 2a. In the corrected-CNT scheme, dimers are being added according to the local corrected CNT rate regardless of the actual critical size, while their prospective sizes in this scheme are very close to these under the direct scheme. In the upstream part of the nucleation region, the actual cluster current calculated for the direct scheme is very high, however, since the critical size there is much higher than two, only a small part of the freshly formed dimers will eventually grow. At a distance of ~2.8 m and upstream the corrected CNT rate and the actual rate are of the same order and the critical size there is very small. Since the prospective-size curves of the two schemes, Fig. 2b, are also very close, the resultant distributions are approximately the same as is seen in Fig. 2a.

The second example we consider is a free expansion of Argon gas from a small nozzle, corresponding to Hagena's experiments on supersonic micro-jets [5]. The nozzle diameter is 0.49 mm, the stagnation pressure and temperature are 2.9 atm and 223 K. In this example, the time for the small volume to travel from the start-condensation region to the region at which collisions cease is of the order of the transient time in CNT so that the

system of differential equations (20) is much stiffer than that in the previous example. To facilitate the convergence of the solution, the Jacobian matrix of the equation system is used [20].
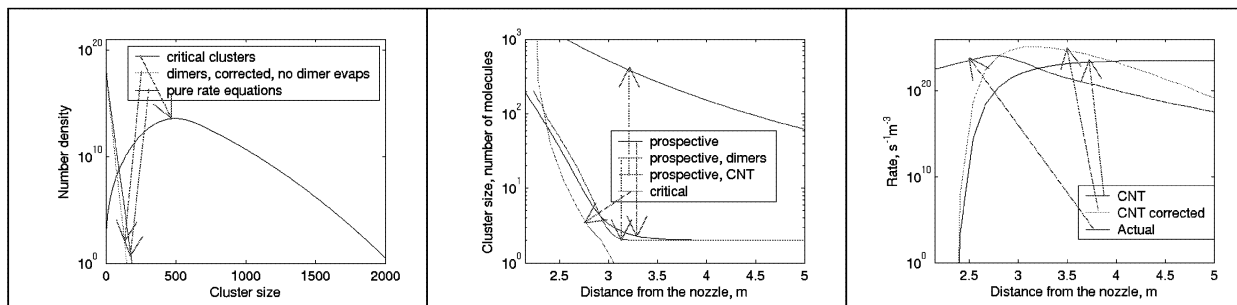


**Fig. 2. A** (left): Terminal cluster distributions for water condensation in a rocket plume. **B** (centre): The prospective size to be reached by a dimer, if evaporation is neglected, as a function of the initial location, and the critical cluster size versus its location. **C** (right): Actual cluster current, calculated for dimer production, and CNT nucleation rates versus the location.
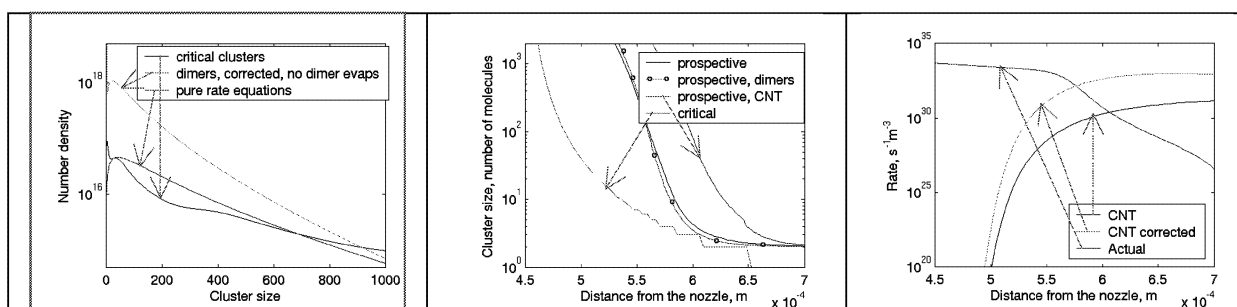


**Fig. 3. A** (left): Terminal cluster distributions for Argon condensation in a supersonic jet. **B** (centre): The prospective size to be reached by a dimer, if evaporations are neglected, as the function of the initial location, and the critical cluster size versus its location. **C** (right): Actual cluster current, calculated for dimer production, and CNT nucleation rates versus the location.

The results are shown in Fig. 3. A comparison of the terminal cluster distributions shown in Fig. 3a reveals that all three strategies provide similar distribution shapes. Both the traditional scheme and the pure rate-equations scheme result in relatively close distributions while the strategy to add dimers results in about order of magnitude larger population of clusters in the size range ~ 2-600. To understand the resultant distributions, the critical cluster size and the prospective size of the introduced dimers are plotted along the jet center line in Fig. 3b, and the CNT-, corrected-CNT and actual cluster currents are depicted in Fig. 3c. For the traditional scheme, the analysis of Fig. 3b and Fig. 3c, similar to that of the water case, reveals that the distribution mode should be about four while another mode at about 40 corresponds to the average prospective size in the region where the CNT current is high (0.60-0.65 mm). At approximately the same region (0.55-0.65) the critical size is small such that the freshly nucleated dimers have a good chance to survive and grow further in the two remaining schemes. Therefore, the two other schemes will produce a distribution mode somewhere between ten and one hundred. Since in most part of this region, the corrected CNT rate is about two orders of magnitude higher than the cluster current calculated under the direct scheme, the corresponding underlying cluster density is also higher in the corrected-CNT case. On the other hand, the average CNT rate in this region is close to the average cluster current, which leads to close resultant number densities as is seen in Fig. 3a.

Concluding this section, we would like to stress that there is no a way to estimate *a priory* the accuracy of the traditional strategy of CNT implementation into modeling of condensation in free gas expansions. The considered two examples may lead to a wrong conclusion that the traditional strategy of CNT implementation is applicable for Argon and not applicable for water. However, our other examples considered elsewhere [21] demonstrate that the degree of discrepancy between the direct and traditional strategy depends on a combination of the initial conditions, such as the orifice diameter, stagnation pressure and temperature, and the material thermodynamic properties, such as the material density, surface tension and temperature dependence of the saturation pressure. Still, the methodology of one-dimensional coupling of rate equations to the gas expansion equations, developed here, can be used to test the applicability of either the traditional or the modified scheme.

# SUMMARY

As is demonstrated in this paper, it is possible to apply the main CNT result – the steady-state nucleation rate to the isobaric/isothermal environment using the correction factor and the strategy to add dimers instead of the critical clusters. However, the steady-state nucleation rate alone cannot be applied for reliable modeling of the coupled condensation – gas expansion processes. The considered examples reveal that even the corrected use of this rate may lead to unpredictable deviations from the correct solution. It is not surprising, therefore, that the predicted by the CNT-rate methodology distribution of Silicon clusters in laser ablation significantly deviates from the experimental distributions [22]. The proposed methodology of coupling between the CNT rate equations and the one-dimensional isentropic gas expansion equations, though very approximate, can be used to test the applicability of either the traditional or the modified scheme in each practical case.

The only way to reliably implement CNT to the modeling of condensation in free gas expansions is via the coupling of the original CNT rate equations to the complete 3-$D$ set of gas dynamics equations, such as the Navier-Stokes equations. Unfortunately, the main advantage of the use of CNT over the more realistic kinetic approach - computational feasibility - will be lost in this case. One way to make the coupled CNT- or kinetic rate equations and gas-dynamics equations computationally feasible is by using a Monte Carlo scheme, e.g., the direct simulation Monte Carlo (DSMC) method.

In principle, DSMC method is capable of including a reasonably large number of interaction types to realistically model the kinetic processes among clusters and monomers, including even such complex reactions as triple collisions. However, these reactions must be characterized in terms of reaction probabilities, cross sections, and energy and angular redistributions prior to their implementation in the DSMC scheme. One way to characterize the reactions is via the Molecular Dynamics (MD) trajectory studies. The development of such hybrid MD-DSMC approach to model the coupled gas expansion and condensation will be one of our future research directions.

# ACKNOWLEDGMENTS

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